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HYBRID TE PANEL TEST RESULTS

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ABSTRACT

Test results are presented for a nine couple (3×3 array) thermoelectric panel of Hybrid thermocouples. In the Hybrid couple, a hollow cylinder of p-type Si-Ge is used to encapsulate a segmented PbTe/Si-Ge n-leg. The Hybrid couple is predicted to offer a 10- to 15-percent improvement in performance relative to all Si-Ge couples. The efficiency, output power, and internal resistance of the panel as well as the resistances of the individual Hybrid couples are presented as a function of test time covering a period of more than 2600 hours. Initial test results indicated Hybrid couple performance consistent with design predictions. Extraneous resistance ranged from 20 to 25% of the Hybrid couple thermoelectric resistance. During the first 600 hours of operation, the degradation rate observed was close to that predicted; however, at that time, the heater failed causing a thermal cycle. An increase in both degradation rate and rate of change of couple resistance was observed following the thermal cycle, and, at 1100 hours, erratic performance of one couple was noted, indicating a partial bond failure. The 10 to 15% improvement over all-Si-Ge couples, demonstrated initially by the Hybrid couple, was offset by the high resistance that developed following the thermal cycle after 600 hours of testing.

LEAD TELLURIDE (PbTe) and silicon-germanium (Si-Ge) alloys are the thermoelectric (TE) materials most often considered for purposes of energy conversion in space. PbTe alloys are characterized by their excellent ability to convert heat to electricity, reflected by the so-called figure-of-merit, for operating temperatures up to about 600°C (873 K). However, for most applications, they must be protected from their environment to prevent degradation due to sublimation. Si-Ge alloys have, for the most part, a somewhat lower figure-of-merit than PbTe, however, their useful temperature range extends up to about 1000°C (1273 K) in air or vacuum, and they are generally superior to PbTe alloys in terms of mechanical strength and machinability.

A unique thermocouple design, proposed by RCA personnel, consists of a segmented Si-Ge/PbTe n-leg and a Si-Ge p-leg. The p-leg is fabricated in the form of a hollow cylinder and is used to encapsulate the segmented n-leg, thereby protecting the PbTe. Such a thermocouple should offer both improved efficiency and stability. Improved stability is predicated on the use of n-type PbTe rather than n-type Si-Ge at temperatures below 540°C (813 K) where the majority of degradation due to precipitation of phosphorus dopant in the Si-Ge is thought to exist. This configuration, called the Hybrid couple, is described in more detail in (1).*

Under Contract NAS3-11843, the RCA Corporation of Harrison, New Jersey, designed and fabricated Hybrid thermocouples for use at a hot-junction temperature of 926°C (1199 K) and an incident heat flux of 2 watts per square centimeter. In order to demonstrate the feasibility of the concept, two TE panels having nine Hybrid thermocouples each, were fabricated (1), instrumented, and delivered to the Lewis Research Center for testing. The predicted Hybrid TE panel performance is presented below:

Number of Hybrid thermocouples	9
Current, ^a A	4.23
Voltage, ^a V	1.66
Power, ^a W	7.0
Efficiency, percent	6.6
Hot shoe area, cm^2	56

*Numbers in parentheses designate References at end of paper.

Temperature, °C (K):

Hot junction	926 (1199)
Intermediate	538 (811)
Cold junction	232 (505)
Incident heat flux, W/cm ²	2.0

^aBased on 1500-hr properties for Si-Ge alloys; also, adjusted for 20% extraneous resistance.

One of the two Hybrid TE panels was endurance tested for 2600 hours at reference design temperatures. The test was conducted to provide a first-order evaluation of the mechanical, thermal, and electrical behavior of the Hybrid couple. The results of this test are presented herein.

DESCRIPTION

HYBRID TE PANEL - The planar Hybrid TE panel consists of nine Hybrid thermocouples arranged in a three-by-three array and electrically connected in series. Photographs of the Hybrid couple and the nine-couple panel are shown in figures 1 and 2, respectively. A sketch of the Hybrid couple is included in figure 3. The overall dimensions of the panel are 7.5 by 7.5 by 7.6 centimeters, resulting in a hot shoe area of 56 square centimeters. Each Hybrid couple consists of a segmented 3N PbTe/70-at. % Si - 30-at. % Ge alloy n-leg and an 80-at. % Si - 20-at. % Ge alloy p-leg. The p-leg is fabricated in the form of a hollow cylinder and used to encapsulate the segmented n-leg. A Si-Mo alloy (85-wt. % Si) heat receptor plate or hot shoe is bonded to the Si-Ge thermoelements at the hot end. At the cold end, the p-Si-Ge and n-PbTe elements are bonded through a cold stack to a copper mounting stud. Copper straps are used to electrically interconnect the couples at the cold end. The thermocouples are mechanically fastened to an aluminum radiator plate. Two intersecting 0.635-centimeter thick copper plates, 15.2 by 15.2 centimeters on a side, are mechanically attached perpendicular to the surface of the aluminum radiator plate to provide the required cooling within the vacuum bell jar. All radiator surfaces are coated with graphite to provide high emittance. Fibrous insulation (Johns-Mansville MIN-K 2020) is used between the thermocouples to minimize shunt heat loss. The gap between the segmented n-leg and the p-leg is filled with 99.5% purity aluminum oxide powder to minimize shunt heat losses through this space.

The p-Si-Ge cylinder is 3.17-centimeters long with a wall thickness of 0.117 centimeter. The n-PbTe

and Si-Ge segment lengths are 0.798 and 1.87 centimeters, respectively. Hot-junction, n-leg-interface and cold-junction temperatures are 926°, 538° and 232° C (1199, 811, and 505 K), respectively.

A more detailed description of both the Hybrid couple and the test panel is given in (1).

INSTRUMENTATION - Each of the 9 Si-Mo hot shoes was instrumented with tungsten - 3% rhenium-tungsten - 25% rhenium thermocouples. The thermocouples were inserted in 0.084-centimeter-diameter holes provided near the corner of each hot shoe and potted in place with an alumina cement. In addition, 10 type K thermocouples were provided between the thermoelectric couples at the cold end (located on the copper connecting straps). The negative legs of these thermocouples were also used as voltage probes. Two copper straps were used, one at each end of the circuit, as power taps.

TEST FIXTURE - The test fixture (fig. 3), consists basically of a double-walled copper box (0.318-cm wall thickness). The heater, contained in the inner box, consist of five strips of 1.27-centimeter-wide graphite tape fastened to a 8.9-centimeter-square, 0.635 ceramic (aluminum silicate) plate. Molybdenum extension leads (0.076 cm diam by 36 cm long) are used between the graphite heater and the external heater leads. Min-K 2020 thermal insulation is used between the heater and the inner box. Four ceramic spacers (0.953 cm in diam and 1.27 cm long) are used to support the inner box from the base of the outer box. The surfaces between the inner and outer boxes are coated with graphite to provide a uniform emittance.

The Hybrid TE panel is placed in the test fixture such that the cold-junction surface is in the plane of the outer wall of the test fixture. The test fixture is mounted on the baseplate of an oil-diffusion-pumped vacuum system with the radiator fins viewing a 45.7-centimeter-diameter glass bell jar.

TESTING PROCEDURE - The nine-couple Hybrid TE panel was tested in the following manner: Room temperature resistance of the entire nine-thermocouple string was measured both before and after installation in the vacuum chamber. The test section was then connected in the load circuit (fig. 4). Three 0- to 2-ohm potentiometers, connected in parallel, were used as the variable-resistance load and a 1-milliohm shunt was used to measure thermoelectric current.

After a vacuum pressure of 10⁻⁴ torr or less was

reached, the heater power was turned on and was gradually increased to achieve operating conditions. Because of the rather large amount of min-K thermal insulation in the vacuum chamber, a relatively slow heatup procedure was used (about 24 hr) to ensure that the vacuum pressure never exceeded 10^{-4} torr (typically 10^{-5} at higher temperatures). When an average hot shoe-temperature of 945°C (1218 K) was reached (corresponding to a hot junction temperature of 928°C (1201 K)) the current and output voltage were recorded and the internal resistance of the panel was determined using the relation:

$$R_i = \frac{V_{oc} - V_L}{I} \quad (1)$$

where V_L is the load voltage, V_{oc} is the instantaneous open-circuit voltage, and I is the current.

The instantaneous open-circuit voltage was measured within 0.2 second after opening the circuit. With the heater input power initially fixed at about 145 watts, the external load was varied slightly, and, after allowing 3 or 4 hours for temperature stabilization, another current-voltage point was recorded. Two such current-voltage points plus the internal panel resistance were recorded periodically thereafter during the subsequent 2600 hours life-test.

Since each of the nine Hybrid couples was instrumented at the cold side with type K thermocouples, it was possible to measure the individual couple output voltages (using the negative leg of each type K thermocouple as a voltage probe) and thereby determine Hybrid couple internal resistance, again using the relation given in equation (1).

The Hybrid TE panel was life-tested with an external resistance adjusted to give a load-to-internal-resistance ratio of about 1.2. The average hot-shoe temperature was determined using only 8 of the 9 W-3Re/W-25Re thermocouples, since one was damaged during installation of the TE panel into the test fixture. The average cold-side temperature was based on nine type K cold-side thermocouples.

There were two shutdowns (one only partial) during the 2600-hour test. The first was due to a system malfunction at 150 hours; the hot-shoe temperature dropped about 300°C , from 945 to 645°C (1218 to 918 K), in about 20 minutes before heater power was restored. The second shutdown occurred at 610 hours due to a heater failure. The TE panel was removed

from the fixture, the heater replaced, and the panel repositioned in the fixture for additional testing.

TEST RESULTS

ELECTRICAL PERFORMANCE - The current-voltage (I-V) characteristics, as well as the resultant output power, recorded at various times during the 2600-hour test, are presented in figure 5. Note that at zero hours the maximum measured power was 7.54 watts at 1.51 volts, which is nearly identical to the interpolated peak power of 7.56 watts at 1.45 volts indicated by the curve. This was typically the case throughout the test, hence "measured" output will be referred to hereafter rather than that derived from the interpolation of data points. Current-voltage characteristics measured at 89 and 257 hours show a drop in maximum power to 7.3 and 7.0 watts, respectively, and, in addition, indicate an increase in Seebeck voltage as evidence by the increase in extrapolated open-circuit voltage. This is consistent with the degradation expected as a result of phosphorus dopant precipitation in the n-SiGe segment between 926° and 538°C (1199 and 811 K). Subsequent I-V traces taken at 572 and 1069 hours exhibit a depression of the I-V curve but no increased open-circuit voltage, suggesting that this degradation is due to a resistance increase alone, with no attendant increase in Seebeck coefficient. This would indicate possible degradation and/or partial separation of some of the metallurgical bonds.

Figure 6 shows the variation in Hybrid couple and panel resistance for a test period in excess of 2600 hours. One partial thermal cycle occurred at about 150 hours (hot-shoe temperature dropped to 645°C (918 K) in 20 min), and a total thermal cycle occurred at about 600 hours (heater failure). Note that seven of the nine couples exhibited resistances in the range of 28 to 30 milliohms between 300 and 600 hours, with some degree of stabilization indicated. Couples #10 and #22 exhibit resistances between 32 and 34 milliohms during the same time interval. The as-fabricated room-temperature resistance of couples #10 and #22 was also on the order of 10% higher than that of the remaining seven couples. A resistance at 1500 hours of 36.6 milliohms was originally predicted for the Hybrid couples. However, the resistivity of the p-type Si-Ge material used for these couples was on the low side, although within acceptable limits. Accordingly, the predicted 1500-hours resist-

ance of the Hybrid couple was adjusted from 36.6 to 30 milliohms. As shown in the figure, only two couples #8 and #17, exhibited the predicted resistance at 1500 hours. Furthermore, the resistance of couple #22 began to fluctuate between 36 and 48 milliohms after 1100 hours of operation, most likely due to an intermittent bond separation. The remaining six Hybrid couples exhibited resistances ranging from 30.7 to 33.4 milliohms at 1500 hours. Between 1500 to 2600 hours, a spreading of the data points is shown with, in general, an increase in the rate of change of resistance. Since the increase is not accompanied by an attendant increase in Seebeck voltage (see fig. 5), it is attributed to the metallurgical bonds rather than the bulk material.

THERMAL PERFORMANCE - The test fixture, described earlier, was instrumented so as to allow calibration with a dummy block in place of the test module. Thus, for a given set of wall temperatures, lead temperatures, etc., it is possible to determine the net heat input to the TE panel. This value varied from 103 to 105 watts. Accordingly, output power and efficiency (power output divided by power input) were determined and plotted against time as shown in figure 7. As indicated earlier, initial panel output power was about 7.5 watts, which exceeds the predicted beginning-of-life power slightly. The corresponding efficiency was 7.2%. After 300 hours of operation, the output power and efficiency appeared to stabilize at 6.75 watts and 6.5 percent, which closely match the 1500-hour predicted values. However subsequent performance data indicated continued degradation, consistent with the attendant increase in couple resistance shown in figure 6. At 2600 hours, the panel output power and efficiency were 5.8 watts and 5.6 percent, respectively. A comparison of the actual performance with that predicted and that of all Si-Ge couples is given in the next section.

COMPARISON OF PREDICTED AND MEASURED PERFORMANCE - Early in the program, Hybrid couple performance was calculated using bond resistance data that was available at that time. This approach resulted in an extraneous resistance (i.e., ratio of non-TE material resistance to TE material resistance) of about 8%. Subsequently, under the AEC-sponsored Multi-Hundred Watt Program, Contract AT(29-2)-2831, an in-depth study of couple resistance was performed and it was concluded that, as a rule-of-thumb, extraneous resistance in an all

Si-Ge couple was about 20%. Hybrid couple performance was therefore recalculated to reflect this increased resistance. This calculated performance is given in the first column of table 1 (all performance is referenced to 1500 hour properties for thermoelectric material). Another adjustment was necessary due to use of the p-type Si-Ge material having a resistivity that was lower than expected. This adjusted performance is given in the second column in table 1. The 1600-hour measured performance of the Hybrid TE panel is given in the third column. The Hybrid couple resistances, presented in the third column, are based on the two best couples from the 9-couple panel. The fact that these couples maintained low resistance during the first 1600 hours of testing, despite the thermal cycles, shows some encouragement for the Hybrid concept. The remaining electrical and thermal performance presented in the third column of table 1 represents average values. Note that the 1600-hour performance is approximately 95% of the predicted value. In view of the variation in performance exhibited by the nine Hybrid couples, the overall performance is quite good at this point. Subsequent degradation, however, decreased performance to 87% of the predicted value at 2600 hours.

Comparison of measured Hybrid couple performance with that of an all-Si-Ge couple is difficult because of a lack of comparable performance data. For purposes of discussion, however, it is interesting to note that a cylindrical all-Si-Ge converter (2) operating at hot- and cold-junction temperatures of 1038 and 342° C (1311 and 615 K), respectively, exhibited an efficiency of less than 6% at 528 hours. Hence, the Hybrid couple has exhibited, at least initially, the potential for achieving similar performance at somewhat lower operating temperature. Obviously, additional testing as well as metallographic examinations will be required to determine whether further modifications and/or improvements are feasible.

SUMMARY OF RESULTS

Performance testing of a nine couple Hybrid TE panel produced the following results:

(1) The initial measured output power and efficiency of the TE panel, in excess of 7.5 watts and 7.2 percent, respectively, were consistent with that estimated in the design analysis for reference design conditions, i.e., average hot junction temperature of 926° C

(1199 K) and average cold junction temperature of 232° C (505 K).

(2) The TE panel exhibited the predicted 10 to 15 percent performance gain over all-Si-Ge couples during the first 600 hours, at which time the heater failed causing a thermal cycle.

(3) After 600 hours of testing, performance degradation increased accompanied by steadily increasing resistance in 6 of the couples and erratic behavior of one of the couples; the two remaining couples exhibited the performance stability anticipated initially. The test was terminated at 2630 hours.

REFERENCES

1. L. P. Garvey, T. R. Krebs, and E. Lee, "Hybrid Thermocouple Development Program," RCA Corp., NASA CR-120875, to be published.
2. Anon., "Multi-Hundred Watt Radioisotope Thermoelectric Generator Program," Progress Report, Oct. through Dec. 1971, General Electric Co., 1971. (Work under Contract AT(29-2)-2831.

Table 1 - Hybrid Thermocouple and Panel Performance

	Predicted values based on 1500 hour properties and 20% extraneous resistance	Predicted values adjusted for low resistivity p-type Si-Ge material	Measured performance (1600 hours)
Resistance, mΩ			
Si-Ge p-leg	16.5	10.0	10 ^a
Si-Ge n-segment	11.5	11.5	14 ^a
PbTe n-segment	2.5	2.5	6 ^a
Extraneous	6.1	6.0	30 ^a
Total	36.6	30.1	
Couple efficiency, %	6.6	6.4	6.2 avg.
Couple power, W	0.78	0.75	0.71 avg.
Couple voltage, V	0.185	0.163	0.17 avg.
Couple current, A	4.23	4.6	4.12 avg.
Panel efficiency, %	6.6	6.4	6.2
Panel power, W	7.0	6.75	6.4
Panel voltage, V	1.66	1.47	1.55
Panel current, A	4.23	4.6	4.12

^aBased on performance of individual couples tested prior to panel testing and the best two couples from the 9-couple panel.

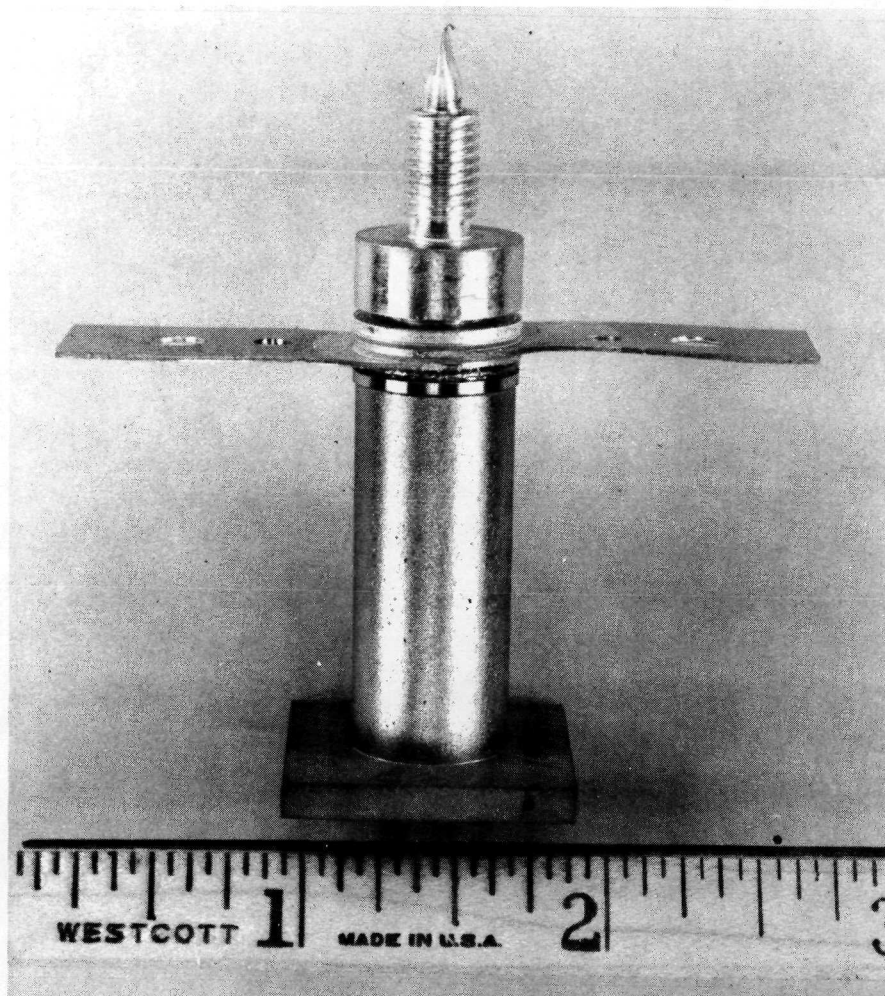


Figure 1. - Hybrid thermocouple.

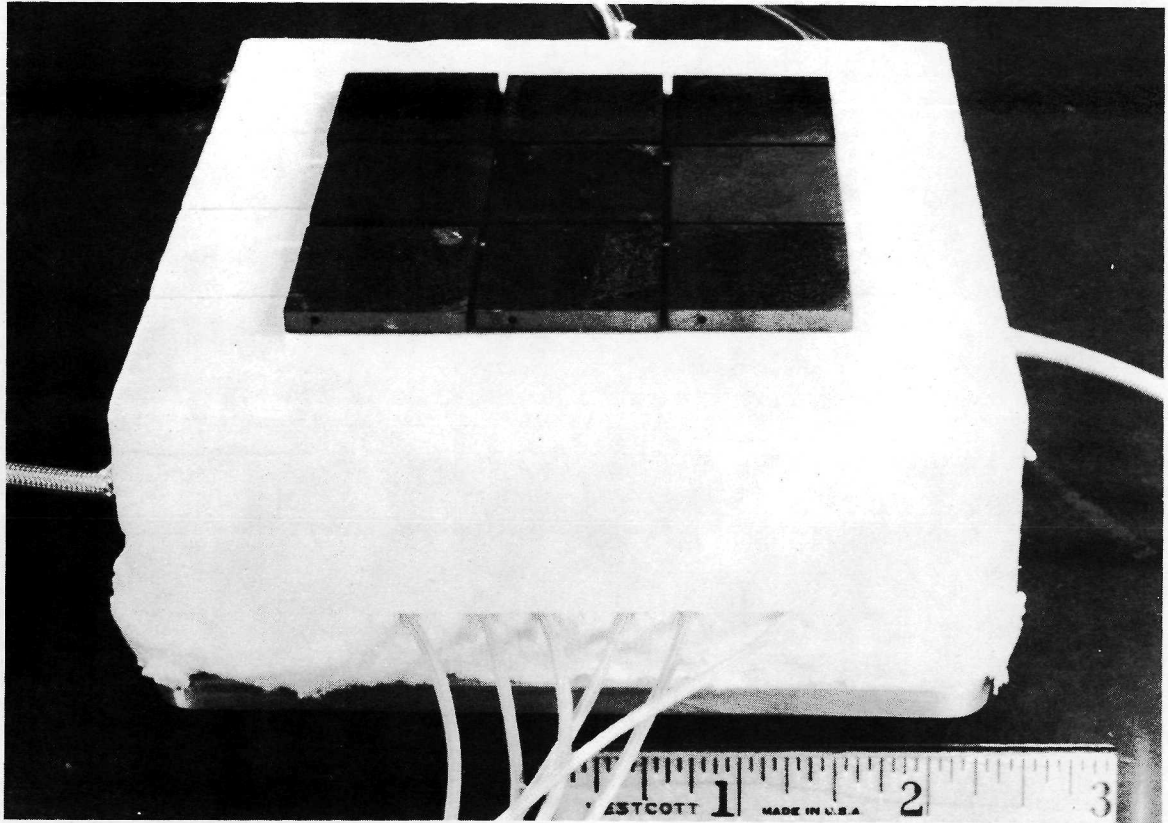
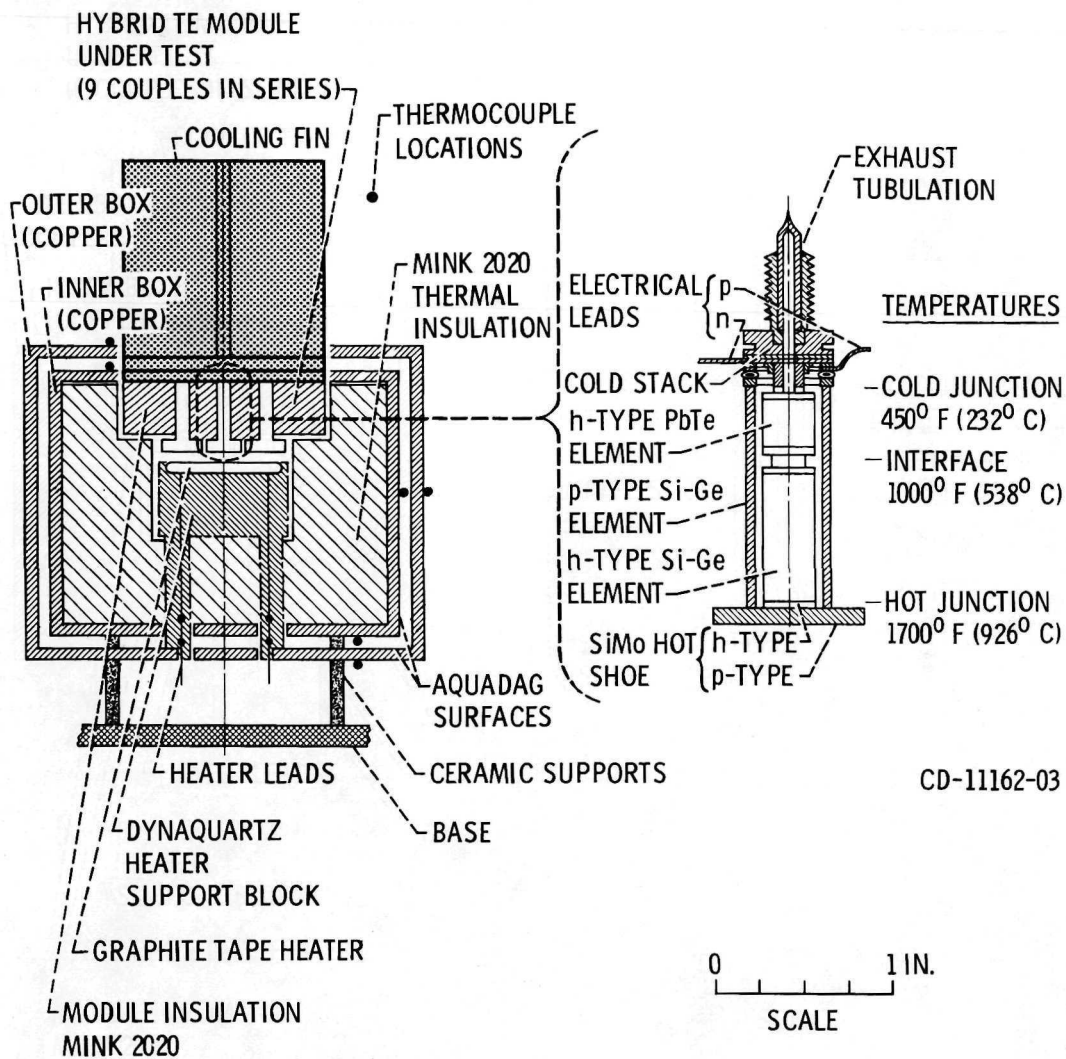


Figure 2. - Nine couple-Hybrid TE panel.



HYBRID EFFICIENCY TESTING DEVICE

HYBRID THERMOCOUPLE

Figure 3. - Hybrid thermoelectric panel test fixture.

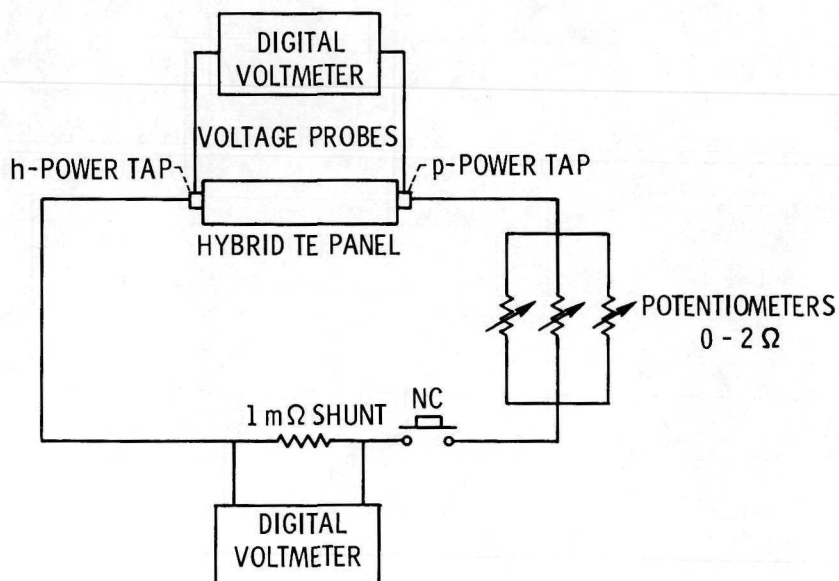


Figure 4. - Schematic of thermoelectric circuit.

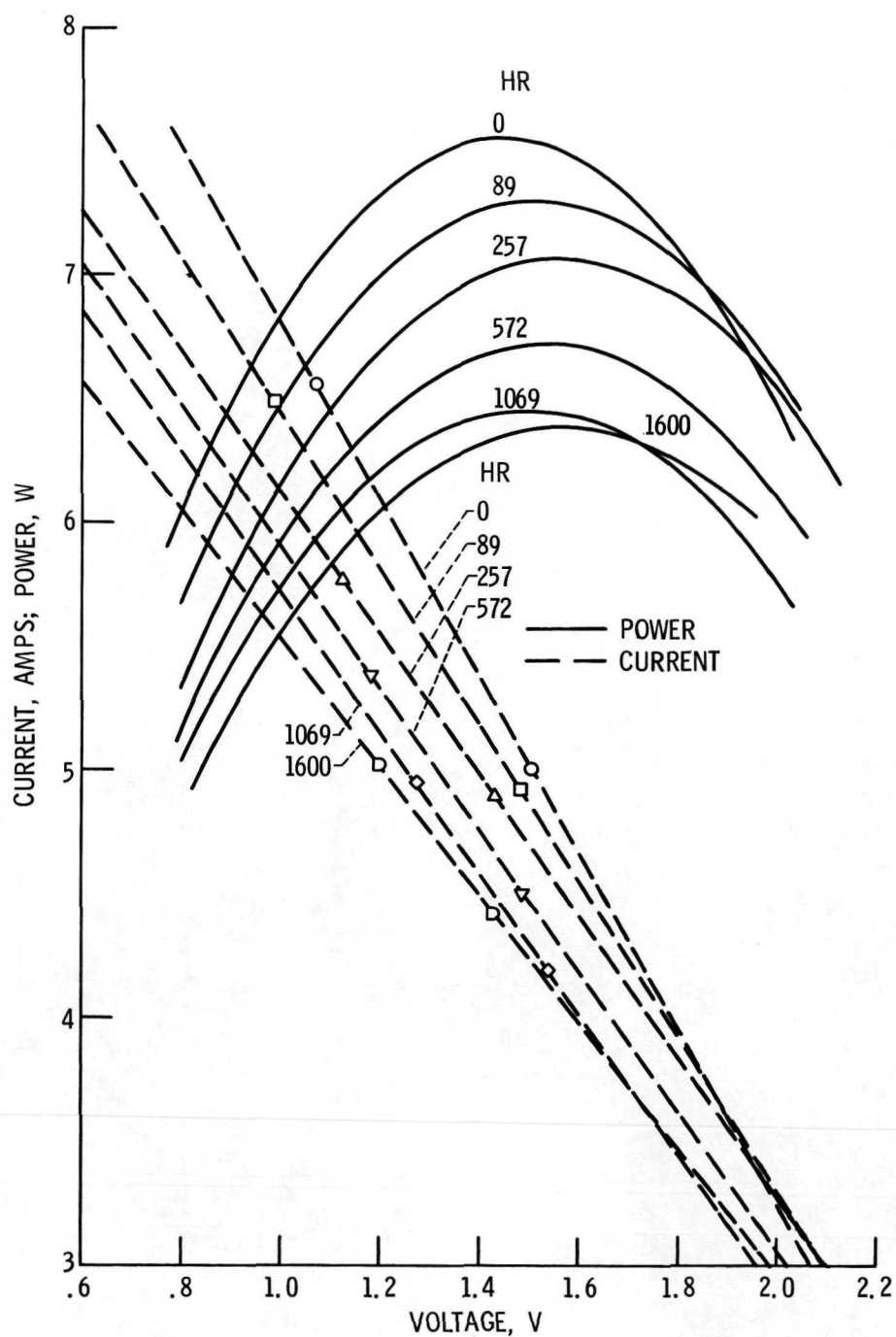


Figure 5. - Variation of current and power with output voltage for Hybrid TE panel number 1.

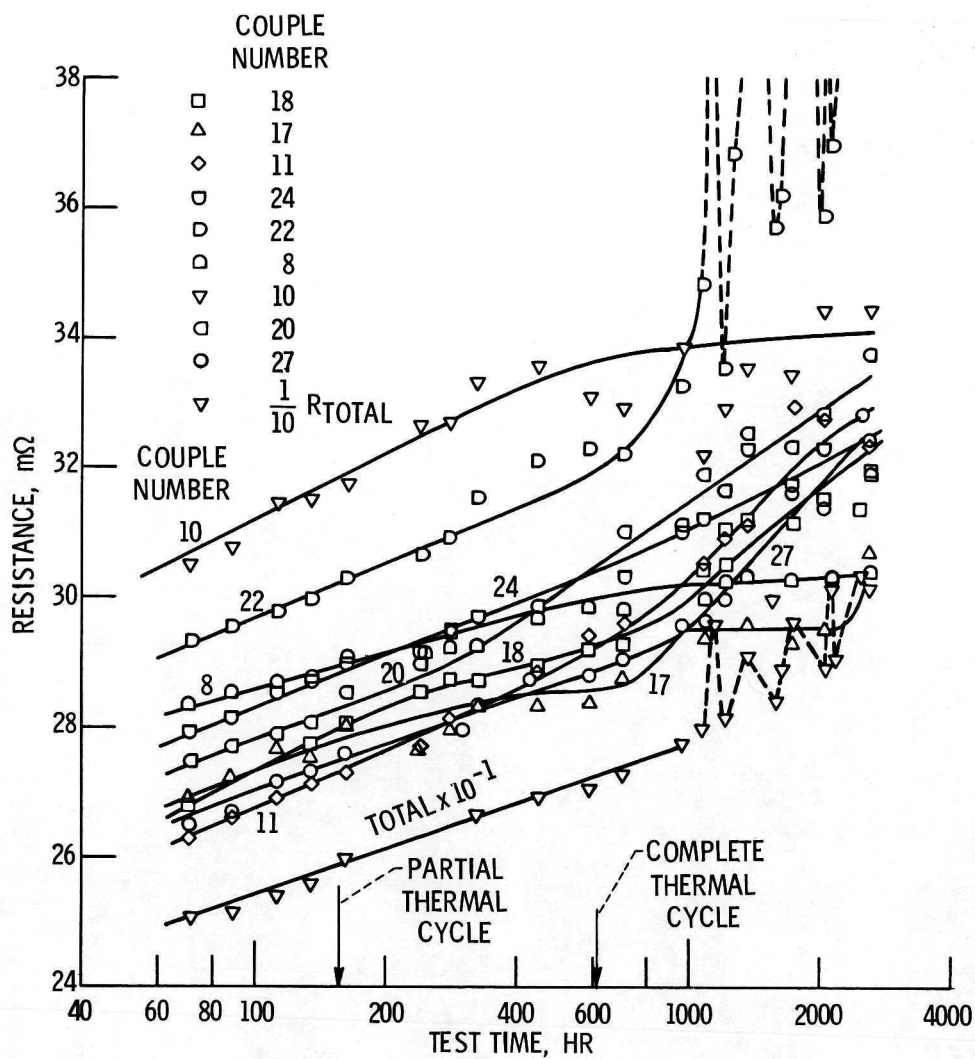


Figure 6. - Resistance plotted against test time.

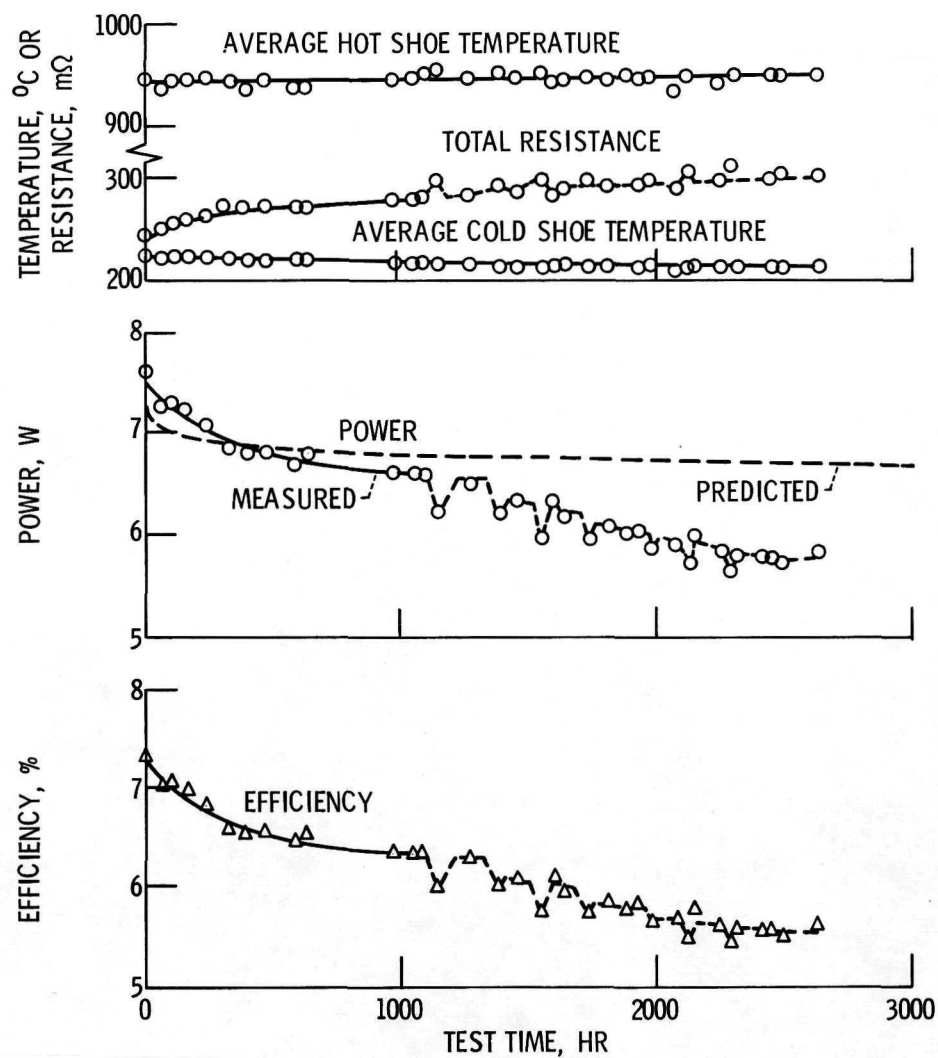


Figure 7. - Hybrid TE panel temperature, resistance, power and efficiency plotted against test time.